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(54) **Detergents for hydrocarbon fuels**

(57) Compounds comprising a Mannich reaction  
product of

a) polyisobutene-substituted alkylated succinimide,  
wherein the alkylated succinimide is derived from a

succinate and an alkylene polyamine;  
b) n aldehyde;  
c) n alkyl substituted phenol.

are disclosed, which are shown to have good detergen-  
cy properties in hydrocarbon fuels.

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## Description

The present invention relates to detergents for use in hydrocarbon fuels. Hydrocarbon fuels generally contain numerous deposit-forming substances. When used in internal combustion engines, deposits tend to form on and around constricted areas of the engine in contact with the fuel. In diesel engines, deposits tend to accumulate in the fuel injection system, thereby hampering good performance of the engine. In automobile engines deposits can build up on engine intake valves leading to progressive restriction of gaseous fuel mixture flow into the combustion chamber and also to valve sticking. It is common practice therefore to incorporate a detergent in the fuel composition for the purpose of inhibiting the formation, and facilitating the removal, of engine deposits, thereby improving engine performance.

US-A-5039307 discloses coupled bis-succinimides, formed by the reaction of an alkenyl bis-succinimide, nonyl-phenol and formaldehyde, for use as detergent additives in diesel fuels. US-A-5039249 discloses the same compounds in gasoline fuels. These compounds are said to reduce intake valve deposits.

We have discovered novel Mannich condensation products of polyisobutene-substituted succinimides, an aldehyde and alkyl substituted phenols which are excellent detergents in fuels. Accordingly in a first aspect the present invention provides a compound comprising a Mannich reaction product of

- a) a polyisobutene-substituted alkylated succinimide, wherein the alkylated succinimide is derived from a succinate and an alkylene polyamine;
- b) an aldehyde;
- c) an alkyl substituted phenol.

A second aspect of the invention provides a fuel composition comprising a major amount of a hydrocarbon fuel, and from 10 to 1000 ppm of the above reaction product.

The polyisobutene (PIB) on the succinimide preferably has a number average molecular weight of from 700 to 2300, preferably from 750 to 1500. It may be derived from a "highly-reactive" PIB, that is one in which at least 70% of the terminal olefinic double bonds are vinylidene, or a "standard" PIB containing a lower proportion of vinylidene double bonds, such as that sold by BP Chemicals under the trade mark Hyvis®.

The alkylated succinimide is the reaction product of a succinate and an alkylene polyamine, which is preferably of the formula  $H-(NRC_xH_y)_n-NH_2$ , where R is H or  $(C_1-C_6)$  alkyl, n is an integer of from 1 to 7, and x is 2 or 3 and y is 4 or 6. Preferred alkylene polyamines are ethylene polyamines ( $R = H$ ,  $x = 2$ ,  $y = 4$ ), particularly ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine.

The aldehyde is preferably a  $(C_1-C_6)$  aldehyde, preferably formaldehyde.

The alkyl substituted phenol is preferably of the formula  $Ph(OH)(R')$ , where  $R'$  represents one or two alkyl groups independently having molecular weights of from 15 to 3000.  $R'$  preferably represents just one alkyl group, para to the OH group, and more preferably a  $(C_3-C_{22})$  alkyl group which may be straight or branched, and which includes alkyl groups derived from propylene oligomers; most preferably  $R'$  is  $-C_{12}H_{25}$  (dodecyl phenol).

Particularly preferred products comprise the reaction product of

- a) a polyisobutene-substituted alkylated succinimide, wherein the alkylated succinimide is derived from a succinate and an ethylene polyamine;
- b) formaldehyde;
- c) dodecyl phenol.

As mentioned above, the compounds of the invention are made by a Mannich reaction involving an alkylated succinimide, aldehyde and a substituted phenol. Hence the aldehyde and phenol can attach to any NH group on the succinimide, although the usual point of attachment is at the terminal  $-NHR$  group. Alkylated succinimides are well known, and the conditions required for Mannich reactions will also be familiar to those skilled in the art. Another aspect of the invention therefore provides a process for producing a compound of Formula (I) above, comprising reacting together a substituted phenol as defined above, an aldehyde, and an alkylated succinimide as defined above, under conditions suitable for a Mannich condensation reaction.

In a further aspect the invention provides an additive package for a fuel composition, comprising from 5 to 30% by weight of a compound as defined above in a solvent comprising an alkoxylated alkyl phenol and optionally other aromatic solvents.

It is preferred that the compound of the invention is present in the fuel composition in the form of an additive package, the package being present at a level of from 200 to 3000ppm, preferably from 600 to 1000ppm. Thus another aspect of the invention provides an additive package for a fuel composition, comprising from 5 to 30% by weight of a compound as defined above, a carrier fluid, and optionally a solvent, preferably an aromatic solvent. Suitable carrier fluids include alkyl phenols, optionally alkoxylated; esters of acids/alcohols, acids/polyols or acids/glycol ethers, the

acids being saturated or unsaturated; phthalate esters; trimellitate esters; alkoxyated alcohols or polyols; polyalkylene glycols; and lubricating oils. Suitable solvents may include most known aromatic or aliphatic hydrocarbons or glycol ethers. The invention also comprises in a still further aspect the use of the above compounds and additive packages as detergents in hydrocarbon fuels.

The hydrocarbon fuel may suitably comprise a hydrocarbon fraction boiling in the gasoline range or a hydrocarbon fraction boiling in the diesel range. Gasolines suitable for use in spark ignition engines, e.g. automobile engines, generally boil in the range from 30 to 230°C. Such gasolines may comprise mixtures of saturated, olefinic and aromatic hydrocarbons. They may be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons. The octane number of the base fuel is not critical and will generally be above 65. In the gasoline, hydrocarbons may be replaced in part by alcohols, ethers, ketones or esters, typically in an amount up to 20% by weight. Alternatively, as the liquid hydrocarbon fuel there may be used any fuel suitable for operating spark compression engines, such as those which may be found in road vehicles, ships and the like. Generally, such a diesel fuel will boil in the range from about 140°C to about 400°C (at atmospheric pressure), particularly in the range from about 150 to 390°C, especially from about 175 to 370°C. Such fuels may be obtained directly from crude oil (straight-run) or from a catalytically or thermally cracked product or a hydrotreated product, or from a mixture of the aforesaid. Alternatively there may be used a biofuel, for example rape seed methyl ester. The cetane number will typically be in the range from 25 to 60.

The fuel composition contains the compound of the invention in an amount sufficient to provide dispersancy. Typically in a gasoline fuel this amount will be in the range from 20 to 1000 ppm w/w based on the total weight of the composition. Typically in a diesel fuel this amount will be in the range from 10 to 500 ppm w/w based on the total weight of the composition.

The fuel composition may suitably be prepared by blending an additive composition comprising a fuel compatible hydrocarbon solvent and the compound of the invention with the hydrocarbon fuel.

The fuel composition in addition to the compound of the invention may contain other known additives. The nature of the additives will depend to some extent on the end-use of the fuel composition. Diesel fuel compositions may contain nitrates or nitrites as a cetane improver, or copolymers of ethylene and/or vinyl esters, e.g. vinylacetate, as a pour point depressant. Gasoline fuel compositions may contain a lead compound as an anti-knock additive and/or an antioxidant, e.g. 2,6-di-tert-butyl phenol, and/or an anti-knock compound other than a lead compound, and/or an additional dispersant, for example a PIB polyamine. The other additives (if any) may be blended directly into the fuel composition or may be incorporated by way of a concentrate composition.

The compounds of the invention may be made by methods well known in the art, using the Mannich condensation reaction. The preferred method is to react an alkyl (usually polyisobutene) succinate with an alkylene polyamine and then use the product in a Mannich reaction with formaldehyde and dodecyl phenol.

The invention will now be further illustrated by reference to the following examples.

#### EXAMPLE 1 - Preparation of polyisobutene succinate/triethylene tetramine adduct

A 2 litre round-bottomed flange flask was charged with 1000g (0.624mol) of a solution of 75% polyisobutene succinate (obtained by reacting the polyisobutene Hyvis® 10, Mw c. 1000, with maleic anhydride) in 25% HAN8572, an aromatic solvent available from Exxon Chemicals. This was heated with stirring to 175°C, following which triethylene tetramine (TETA) (79.4g, 0.543mol) was added dropwise using a pressure equalising funnel over 35 minutes. The reaction mixture was then heated at 175°C for a further four hours. The resulting product was filtered through a 12mm Celite pad whilst still warm, and analysed. The product was found to be 71.8% pure, with a nitrogen content of 2.75% (theoretical 2.85%).

#### EXAMPLE 2 - Preparation of adduct of polyisobutene succinate triethylene tetramine (TETA) formaldehyde and dodecyl phenol

The product of Example 1, in the form of a 75% solution in 25% HAN8572, was charged to a 500ml round-bottomed flask (173.1g, 0.1mol), together with paraformaldehyde (3.0g, 0.1mol) and dodecyl phenol (26.8g, 0.1mol), together with 100g of toluene as solvent. The reaction mixture was heated rapidly to 100°C and then to 127°C as distillation occurred over 90 minutes. The mixture was then held at 127°C for a further three hours. 1.8ml of water was collected. The product was then transferred to a 500ml Florentine flask and stripped of toluene on a rotary evaporator at 80°C/29"Hg. The product was then filtered warm through a 12mm Celite pad. The product was found to be 68.2% pure, with a nitrogen content of 2.22% (theoretical 2.37%).

EXAMPLE 3 - Preparation of adduct of polyisobutene succinate ethylene diamine (EDA), formaldehyde and dodecyl phenol

The procedure and reactants of Examples 1 and 2 were followed, except that instead of triethylene tetramine, 32.6g (0.543mol) of ethylene diamine (EDA) was used in the first stage, and then 161.6g (0.1ml) of the resultant product as a 75% solution in 25% HAN8572 was used in the Mannich reaction. Analysis revealed 1.15% nitrogen, alkalinity value of 7.5 mgKOH g<sup>-1</sup>.

EXAMPLE 4 - Preparation of adduct of polyisobutene succinate diethylene triamine (DETA), formaldehyde and dodecyl phenol

The procedure and reactants of Examples 1 and 2 were followed, except that instead of triethylene tetramine, 56.02g (0.543mol) of diethylene triamine (DETA) was used in the first stage, and then 167.4g (0.1 ml) of the resultant product as a 75% solution in 25% HAN8572 was used in the Mannich reaction. Analysis revealed 1.72% nitrogen, alkalinity value of 24.3 mgKOH g<sup>-1</sup>.

EXAMPLE 5 - Preparation of adduct of polyisobutene succinate tetraethylene pentamine (TEPA), formaldehyde and dodecyl phenol

The procedure and reactants of Examples 1 and 2 were followed, except that instead of triethylene tetramine, 102.8g (0.543mol) of tetraethylene pentamine (TEPA) was used in the first stage, and then 178.8g (0.1ml) of the resultant product as a 75% solution in 25% HAN8572 was used in the Mannich reaction. Analysis revealed 2.91% nitrogen, alkalinity value of 64.8 mgKOH g<sup>-1</sup>.

ENGINE TESTS

The compounds prepared in the Examples above were evaluated as detergency additives in fuels according to a standard engine test, following method CEC F-05 A-93 on a Mercedes Benz M 102.982 engine. The fuel employed was unleaded CEC RF 83-A-91, and the oil RL-189/1. The compounds tested were incorporated in an additive package with the following formulation:

paradodecylphenol/propylene oxide (11:1 mol ratio) carrier	- 37.9% by weight
HAN 8572 (Exxon Chemicals) aromatic solvent	- 37.2% by weight
additive of Examples 2-5	- 24.9% by weight

The package was dosed in the fuel at 800ml/m<sup>3</sup>.

Measurements were made of the inlet valve deposits, and the valves were also given a visual rating. In this test a visual rating of 9.5 or greater is considered to be a good result.

TABLE 1

EXAMPLE	DEPOSITS (mg)	AVE. VISUAL RATING
no additive package	278	7.59
2 (TETA)	3	9.87
3 (EDA)	109	8.42
4 (DETA)	33	9.37
5 (TEPA)	10	9.70

These results show that the triethylene tetramine (TETA) adduct is the best fuel detergent, and the TEPA adduct is also considered very good.

Claims

- Compound comprising a Mannich reaction product of

- a) a polyisobutene-substituted alkylated succinimide, wherein the alkylated succinimide is derived from a succinate and an alkylene polyamine;
- b) an aldehyde;
- c) an alkyl substituted phenol.

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2. Compound according to claim 1 wherein the polyisobutene has a number average molecular weight of from 700 to 2300, preferably from 750 to 1500.

3. Compound according to claim 1 or 2 wherein the aldehyde is a (C<sub>1</sub>-C<sub>6</sub>) aldehyde, preferably formaldehyde.

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4. Compound according to any preceding claim wherein the alkylene polyamine is of the formula  $H-(NRC_xH_y)_n-NH_2$ , where R is H or (C<sub>1</sub>-C<sub>6</sub>) alkyl, n is an integer of from 1 to 7, and x is 2 or 3 and y is 4 or 6.

5. Compound according to claim 4 wherein the alkylene polyamine is an ethylene polyamine (R = H, x = 2, y = 4), preferably ethylene diamine, diethylene triamine, triethylene tetramine or tetraethylene pentamine.

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6. Compound according to any preceding claim wherein the alkyl substituted phenol is of the formula Ph(OH)(R'), where R' represents one or two alkyl groups independently having molecular weights of from 15 to 3000.

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7. Compound according to claim 6 wherein R' represents one alkyl group para to the OH group, preferably a (C<sub>3</sub>-C<sub>22</sub>) alkyl group which may be straight or branched, and which includes alkyl groups derived from propylene oligomers; most preferably -C<sub>12</sub>H<sub>25</sub>.

8. Additive package comprising from 5 to 30% by weight of a compound according to any preceding claim, a carrier fluid, preferably an alkoxylated alkyl phenol, and a solvent, preferably an aromatic solvent.

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9. Composition comprising a hydrocarbon fuel, preferably a gasoline or diesel fuel, and a compound or additive package according to any preceding claim, wherein the concentration of said compound in the fuel is from 10 to 1000ppm by weight.

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10. Process for producing a compound as defined in any of claims 1 to 7, comprising reacting together an alkyl substituted phenol, an aldehyde, and an alkylated succinimide derived from a succinate and an alkylene polyamine, under conditions suitable for a Mannich condensation reaction.

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11. Use of a compound or additive package according to any of claims 1 to 8 as a detergent in a hydrocarbon fuel.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 6630

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 699 724 A (NALESNIK ET AL.) * claims 1-3,8,12 *	1-7,10	C10L1/22 C10L1/14 C10L10/00
X	GB 2 017 108 A (OROBIS) * claims 1-8 *	1-7,10	
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D,X	US 5 039 307 A (HERBSTMAN ET AL.) * the whole document *	1-7,9-11	
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A	US 4 533 361 A (SUNG ET AL.) * column 7, line 1 - line 22 *	1-11	
A	EP 0 545 653 A (ETHYL) * page 15, line 48 - line 50; claim 12 *	1-11	
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		9 December 1997	De La Morinerie, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background Q : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date O : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			





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Application Number  
EP 97 30 6630

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 647 700 A (ETHYL) * page 5, line 24 - line 35 *	8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 December 1997	Examiner De La Morinerie, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application C : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			